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# Jewellery — Determination of silver in 999 $^{0}/_{00}$ silver jewellery alloys — Difference method using ICP-OES

*Joaillerie, bijouterie — Dosage de l'argent dans de l'argent 999 $^{0}/_{00}$ — Méthode de la differénce utilisant ICP OES*

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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 174, *Jewellery*.

This second edition cancels and replaces the first edition (ISO 15096:2008), which has been technically revised with the following changes:

a) change in the scope that this method is the referee method;

b) addition of silver and silver nitrate in Clause 5;

c) addition of a warning in Clause 7 that suitable health and safety procedures should be followed;

d) change of sample solution in 7.1;

e) split of 7.2 "Calibration solution" into 7.2 "Silver matrix calibration solutions" and 7.3 "Aqua regia matrix calibration solutions";

f) change of 8.2 "Method of calculation";

g) change of repeatability to 0,1 ‰;

h) amendment of wavelengths in Table A.1;

i) standard editorially revised.

# Introduction

The following definitions apply in understanding how to implement an ISO International Standard and other normative ISO deliverables (TS, PAS, IWA).

- "shall" indicates a requirement;
- "should" indicates a recommendation;
- "may" is used to indicate that something is permitted;
- "can" is used to indicate that something is possible, for example, that an organization or individual is able to do something.

ISO/IEC Directives, Part 2 (sixth edition, 2011), 3.3.1 defines a requirement as an "expression in the content of a document conveying criteria to be fulfilled if compliance with the document is to be claimed and from which no deviation is permitted."

ISO/IEC Directives, Part 2 (sixth edition, 2011), 3.3.2 defines a recommendation as an "expression in the content of a document conveying that among several possibilities, one is recommended as particularly suitable without mentioning or excluding others, or that a certain course of action is preferred, but not necessarily required, or that (in the negative form) a certain possibility or course of action is deprecated, but not prohibited."

# Jewellery — Determination of silver in 999 $^{0}/_{00}$ silver jewellery alloys — Difference method using ICP-OES

## 1 Scope

This International Standard specifies the analytical procedure for the determination of silver with a nominal content of at least 999 ‰ (parts per thousand) by measuring specific elements listed in Table A.1.

This International Standard specifies a method intended to be used as the recommended method for the determination of fineness in 999 ‰ silver alloys covered by ISO 9202.

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11596, *Jewellery — Sampling of precious metal alloys for and in jewellery and associated products*

## 3 Principle

The sample is weighed and dissolved in nitric acid to prepare a 10 g/l solution. The suspension, which can be present in that solution, is isolated by centrifugation and dissolved in aqua regia. Both solutions are analysed separately by ICP-OES and the total content of each impurity in the sample is obtained by adding together the results of the two analyses. The silver content is obtained by subtraction of the total content of impurities in the sample from 1 000 ‰.

## 4 Sampling

The sampling procedure shall be performed in accordance with ISO 11596.

## 5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

**5.1 Hydrochloric acid** (HCl), approximately 30 % to 37 % HCl (mass fraction).

**5.2 Nitric acid** ($HNO_3$), approximately 65 % to 70 % $HNO_3$ (mass fraction).

**5.3 Stock solution 1** (shall not contain any chloride), all elements given in Table A.1 (100 mg/l each) in 1 mol/l $HNO_3$ (5.2). The solution should be prepared just before use.

**5.4 Stock solution 2** (may contain both chlorides and nitrates), Al, Au, Cr, Fe, Mg, Ni, Pt, and Sn (100 mg/l each) in 1 mol/l HCl (5.2) or $HNO_3$ (5.3). The solution should be prepared just before use.

**5.5 Aqua regia** (should be prepared just before use).

Mix three volumes of hydrochloric acid (5.2) and one volume of nitric acid (5.3).

**5.6 Silver**, of 999,9 ‰ minimum or;

**5.7 Silver nitrate**, of photographic quality.

# 6 Apparatus

**6.1 Customary laboratory apparatus**.

**6.2 ICP OES**, with

— fixed and/or scanning channels,

— optical resolution of 0,02 nm for the relevant elements and a detection limit of 0,05 mg/l or better, and

— capability of background correction.

NOTE For preferably used wavelength, see Annex A.

**6.3 Analytical balance**, with a reading accuracy of 0,1 mg.

**6.4 Centrifuge**, suitable for 10 ml to 50 ml tubes and rotating at 3 000 r/min (revolution per minute) or more.

# 7 Procedure

**WARNING — Suitable health and safety procedures should be followed.**

## 7.1 Sample solution

Each sample has to be analysed twice and shall be prepared as follows.

Weigh approximately 500 mg of the sample portion to the nearest 0,1 mg, transfer into a 50 ml beaker, and add 7,5 ml of $H_2O$ and 7,5 ml of $HNO_3$ (5.2). Heat gently until complete dissolution of the sample and continue to heat to expel the nitrogen oxides. Add 10 ml of water. After cooling to room temperature, transfer the solution from the 50 ml beaker to the centrifuge tube. Centrifuge the mixture at 3 000 r/min for 5 min and transfer the liquid phase into a 50 ml volumetric flask. Add 5 ml of water to the residue, centrifuge the mixture again at 3 000 r/min for 5 more minutes, and add the newly formed liquid phase to the 50 ml volumetric flask. This operation is repeated for three times. Make up the volume of the solution with water to 50 ml. Analyse this solution without delay using the calibration solutions specified in 7.2.

Add 2 ml of freshly prepared aqua regia (5.5) to the residue after centrifugation. Heat at 80 °C for 2 h. Cool to room temperature, transfer to a 5 ml volumetric flask, rinse with water, and make up with water to 5 ml. Analyse this solution using the aqua regia calibration solutions specified in 7.3.

## 7.2 Silver matrix calibration solutions (10 g/l)

**Blank solution 1**. Weigh approximately 500 mg of silver (5.6) or approximately 787 mg of silver nitrate (5.7) and dissolve as specified in 7.1. Allow to cool and make up to 50 ml with water and mix thoroughly.

**Calibration solution 1**. Weigh approximately 500 mg of silver (5.6) or approximately 787 mg of silver nitrate (5.7) and dissolve as specified in 7.1. Allow to cool and add 2,5 ml of the stock solution 1 (5.3) and make up the solution up to 50 ml with water and mix thoroughly. This solution is unstable and should be prepared just before use.

### 7.3 Aqua regia matrix calibration solutions

**Blank solution 2**. Transfer 20 ml of aqua regia (5.5) into a 50 ml volumetric flask. Make up to 50 ml with water and mix thoroughly.

**Calibration solution 2**. Transfer 20 ml of aqua regia (5.5) into a 50 ml volumetric flask, add 2,5 ml of the stock solution 2 (5.4), make up to 50 ml with water, and mix thoroughly.

### 7.4 Measurements

Set up the instrument in accordance with the manufacturer's instructions and choose appropriate background correction positions. A clean torch, spray chamber, and sample uptake tubes shall be used and the plasma shall be stabilized also before use, following the recommendations of the instruments manufacturer.

Spray the calibration solutions 1 and 2 in accordance with the defined instrument calibration procedure and then run the analytical procedure for the sample solutions. The result shall be displayed with enough decimal places to provide an accurate indication of concentrations at the detection limits of the relevant elements.

Each solution shall have a stabilization time of at least 30 s followed by five integrations of at least 5 s each for the determination of the net intensities (i.e. background-corrected).

The rinsing time between each measurement shall be sufficient to allow the signal of each impurity to come back to the baseline.

Each analysis (silver 10 g/l and aqua regia) has to be carried out separately with the calibration solutions specified in 7.2 and 7.3.

## 8 Calculation and expression of results

### 8.1 Calibration curves

Calculate the calibration curves for each element using the blank solutions and the calibration solutions.

### 8.2 Calculation

By means of the calibration curves (see 8.2), convert the net intensity values into concentration values for both analyses in silver 10 g/l matrix and aqua regia matrix using Formula (1) to calculate the mass ratio of each relevant element ($W_\text{i}$).

$$W_\text{i} = \frac{c_{\text{i,Ag}} \times V_{\text{s,Ag}}}{m_\text{s}} + \frac{c_{\text{i,ar}} \times V_{\text{s,ar}}}{m_\text{s}} \quad (1)$$

where

| | |
|---|---|
| $c_{\text{i,Ag}}$ | is the concentration of element *i* in the silver (10 g/l) matrix sample solution, in mg/l; |
| $V_{\text{s,Ag}}$ | is the volume of the silver (10 g/l) matrix sample solution, in litres (0,05 l as defined in 7.1); |
| $c_{\text{i,ar}}$ | is the concentration of element *i* in the aqua regia matrix sample solution, in mg/l; |
| $V_{\text{s,ar}}$ | is the volume of the aqua regia matrix sample solution, in litres (0,005 l as defined in 7.1); |
| $m_\text{s}$ | is the mass of the metallic sample, in milligrams. |

The detection limit is defined as three standard deviations of the concentration of each individual element measured in the blank solution for the corresponding matrix.

The silver fineness ($W_{sp}$), expressed in parts per thousand (‰), is thus calculated using Formula (2):

$$W_{sp} = 1\,000 - \left( \sum w_i \times 1\,000 \right) \tag{2}$$

where

$\Sigma w_i$ is the sum of the mass portion of each element found above its detection limit.

### 8.3 Repeatability

The results of duplicate determinations shall not deviate more than 0,1 ‰ of the precious metal fineness. If the variation is greater than this, the assay shall be repeated.

## 9 Test report

The test report shall include at least the following information:

a) identification of the sample including source, date of receipt, form of sample;

b) sampling procedure;

c) the method used by reference to this International Standard, i.e. ISO 11490;

d) precious metals content of the sample, in parts per thousand (‰) by mass, as single values and mean values, with the result reported with four significant figures;

e) if relevant, any deviations from the method specified in this International Standard;

f) any unusual features observed during the determination;

g) date of test;

h) identification of the laboratory carrying out this analysis;

i) signature of the laboratory manager and operator.

# Annex A
(normative)

# Wavelengths

Other wavelengths than those specified in Table A.1 can be used. In such cases, attention shall be paid to spectral interferences. This table is not exhaustive. If other elements are present, they shall be analysed.

**Table A.1 — Silver**

| Element | Wavelength nm | Alternative nm | Element | Wavelength nm | Alternative nm |
|---|---|---|---|---|---|
| Al | 396,152 | | Ni | 231,604 | 352,454 |
| As | 193,759[a] | | Pb | 220,353 | 168,220 |
| Au | 267,595 | 242,795 | Pd | 340,458 | 360,955 |
| Bi | 223,061 | | Pt | 265,945 | 306,471 |
| Cd | 228,802 | 226,502 | Sb | 206,833 | 217,581 |
| Co | 228,616 | 238,892 | Se[b] | 196,090 | 203,985 |
| Cr | 205.560 | 283,563 | Si[c] | 251,611 | |
| Cu | 324,754 | | Sn | 189,989 | |
| Fe | 259,940 | | Te | 214,281 | 238,578 |
| Mg | 280,270 | 285,213 | Ti | 336,121 | |
| Mn | 260,569 | 257,610 | Zn | 206,200 | 213,856 |

[a] The used wavelength depends on the type of apparatus, e.g. 193,695 is also commonly used for As.

[b] The used wavelength depends on the type of apparatus, e.g. 196,026 is also commonly used for Se.

[c] All vessels and reagent bottles shall be PTFE or plastic.